APPLICATION OF THE SYNCHROSCAN STREAK CAMERA TO REAL TIME PICOSECOND MEASUREMENTS OF MOLECULAR ENERGY TRANSFER

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ABSTRACT

Using the continuously operating "Synchroscan" streak camera (time resolution 3 - 5 psec) in conjunction with the synchronous excitation pulses from a C.W. mode locked dye laser, singlet - singlet resonance energy transfer from DODCI (donor) to malachite green (acceptor) or to DQOCI in ethanolic solution has been investigated. For a fixed donor concentration of $10^{-4}$ M, various acceptor concentrations from $10^{-5}$ M to $7.5 \times 10^{-3}$ M were studied, and the critical transfer distance $R_c$ determined to have average values of 45.6 Å and 61.8 Å for malachite green and DQOCI respectively.

INTRODUCTION

In the mode-locking of the C.W. rhodamine 6G dye laser it has been reported (1) that the addition of malachite green ($4,4'$ tetramethyldiaminotriphenylmethane chloride) or DQOCI ($1,3'$ diethyl $4,2'$ quinolyloxacarbocyanine iodide) to the more commonly used saturable absorber DODCI ($3,3'$ diethyloxadicarbocyanine iodide) can lead to increased stability of operation well above threshold (1,2,3). Resonant transfer of excited electronic state energy has been suggested as a mechanism to explain the above observation (4), and a study of this is interesting from the point of the mode-locking process. The "Synchroscan" streak camera greatly facilitates the carrying out of these excitation energy transfer measurements, since complete fluorescence decay profiles can be recorded at repetition rates of $\sim 140$ MHz with a time resolution limit of $\sim 3$ psec. In addition, low peak power picosecond pulses ($\sim 200$ W) from a C.W. mode-locked dye laser operating in synchronism are utilized for excitation, thus avoiding non-linear effects in the sample.

EXPERIMENTAL

The experimental arrangement is shown schematically in figure 1. A synchronously pumped mode locked C.W. rhodamine 6G dye laser (5) was the source of the picosecond excitation pulses. Calibration and linearity of the streak was checked using the
The train of excitation pulses was focused using lens L₁ (f = 7.5 cm) into the sample cell C. Typical maximum peak power densities ~5 MW cm⁻² were used. The fluorescence detected at 90° with respect to the incident beam was passed through a polarizer P set at 54.7° to eliminate any distortional effect on the recorded fluorescence profiles due to fluorescence depolarization arising from rotational diffusion (6). After collection and collimation the light was passed through a monochromator (bandwidth 1.5 nm) and the selected fluorescence was directed with lens system L₃ on to the slit S of the streak camera, where it was focused on to the S20 photocathode of the Photochron II streak tube in the usual manner (2).

Synchronism of the repetitive sinusoidal ramp voltage driving the deflection plates of the camera was achieved by directing a percentage (~5%) of the mode locked dye laser output, off beam splitter BS₁, on to a fast photodiode. The resulting electrical signal triggered a tunnel diode oscillator, the output of which at 140 MHz, was amplified to produce the driving voltage. In this way successive streaked images were precisely superimposed at the 140 MHz repetition rate while maintaining time resolution down to 3 psec. The deviation from linearity is better than 3% and the camera has demonstrated a dynamic range of $1 \times 10^3$. Using an optical multichannel analyser lens coupled to the streak camera phosphor, integration and storage of the recorded image for subsequent display on a chart recorder CR was possible.

The excitation wavelength was set to 575 nm and the peak of the bandpass of the monochromator to 615 nm (just below the fluorescence peak of the normal isomeric form of DODCI). In the absence of acceptor molecules a recorded fluorescence lifetime of a $10^{-4}$ M ethanolic solution of DODCI gave 1150 ± 40 psec which is in good agreement with previously reported values (7,8). Addition of a $10^{-5}$ M solution of malachite green in ethanol to the DODCI reduced the recorded fluorescence lifetime to 1060 psec, and further increase in the malachite green concentration correspondingly led to a more pronounced decrease in the DODCI lifetime. This can be seen in figure 2 and the recorded lifetimes are listed in table I. Addition of DQOCI led to a similar effect.

The shortening due to DQOCI was greater than with malachite green due to the larger
Fig. 2. Recorded fluorescence profile of $10^{-4}$ M DODCI in ethanol with (a) 0, (b) $10^{-5}$ M, (c) $10^{-4}$ M, (d) $10^{-3}$ M, (e) $2.5 \times 10^{-3}$ M and (f) $7.5 \times 10^{-3}$ M malachite green acceptor.

Table I

<table>
<thead>
<tr>
<th>Acceptor Concentration</th>
<th>Malachite Green $\tau$ (psec) $R_0$ (Å)</th>
<th>DQOCI $\tau$ (psec) $R_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1148$</td>
<td>$1036$</td>
</tr>
<tr>
<td>$1 \times 10^{-5}$ M</td>
<td>$1060$</td>
<td>$965$</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>$982$</td>
<td>$814$</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>$961$</td>
<td>$751$</td>
</tr>
<tr>
<td>$2.5 \times 10^{-4}$</td>
<td>$921$</td>
<td>$697$</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>$862$</td>
<td>$582$</td>
</tr>
<tr>
<td>$7.5 \times 10^{-4}$</td>
<td>$811$</td>
<td>$555$</td>
</tr>
<tr>
<td>$1 \times 10^{-3}$</td>
<td>$751$</td>
<td>$-2$</td>
</tr>
<tr>
<td>$2.5 \times 10^{-3}$</td>
<td>$510$</td>
<td>$-2$</td>
</tr>
<tr>
<td>$5 \times 10^{-3}$</td>
<td>$434$</td>
<td>$-2$</td>
</tr>
<tr>
<td>$7.5 \times 10^{-3}$</td>
<td>$260$</td>
<td>$-2$</td>
</tr>
</tbody>
</table>

Where Förster kinetics of energy transfer are applicable (9, 10) the modified form of the time evolution of the fluorescence intensity is written

$$I_D(t) = I_D(0)\exp\left(-\frac{t}{\tau}\right)\exp\left(-2\gamma\left(\frac{t}{\tau}\right)^3\right)$$
where \( \tau \) is the fluorescence lifetime in the absence of excitation energy transfer and \( \gamma = C_A/C^0 \), and \( C^0 \) is the acceptor concentration with \( C_A \) the critical concentration given by \( 3000/2N^3R_0^3/N_R^3 \). \( N \) is Avogadro's number and the critical transfer distance \( R_0 \) is defined as the distance at which non radiative dipole-dipole energy transfer has the same probability as the sum over all other de-excitation processes of the donor excited state. A graph of \( \log_{10} I_D(t)/I_F(t) \) against \( t^{1/2} \), where \( I_F(t) \) is the unquenched fluorescence profile and \( I_F(t) = I_F(o)\exp(-t/\tau) \), should give a straight line dependence of gradient \( -2\gamma/2.303 \tau^{1/2} \). Such a plot is shown in figure 3 where the number of points has been reduced for clarity, and relates to a 5 x 10^{-4} M malachite green acceptor concentration.

![Fig. 3. Log_{10}[I_D(t)/I_F(t)] versus t^{1/2} for a 5 x 10^{-4} M malachite green acceptor concentration.](image)

From table I it can be seen that the value of \( R_0 \) tends to level out at higher concentrations of acceptor. The unrealistically high \( R_0 \) values for the lower concentrations may be due to the excitation energy transfer rate (which varies as \( R^{-6} \)) becoming small at these lower concentrations and the decay of the excited state is not so well defined by the modifying term \( (2\gamma(t/\tau)^{3/2}) \) in the Förster expression. The deviation of the experimentally recorded fluorescence profiles from the Förster theoretically predicted computed curves can be seen in figure 4. For a 2.5 x 10^{-3} M malachite green acceptor concentration, agreement is quite good. However, at lower concentrations deviation between theory and experiment is quite apparent (see figure 4(b) for example for a 10^{-5} M malachite green acceptor concentration), indicating that the correction factor introduced by the Förster theory is not valid in this region. Using the five highest values of acceptor concentration used, an average value for \( R_0 \) of 45.6 Å and 61.8 Å were obtained for malachite green and DQOCI respectively.
In addition the results show that resonance energy transfer should not play a major role in the mode locking process at the typical dye concentrations used in practice.

Fig. 4. Experimental and computed curves, assuming Förster kinetics, of fluorescence decay of $10^{-4}$ M DODCI with (a) $2.5 \times 10^{-3}$ M and (b) $10^{-5}$ M malachite green added.

The ability of the synchroscan streak camera to resolve small changes in fluorescence lifetimes under low power excitation greatly facilitates these direct measurements of resonance energy transfer with picosecond resolution, and should therefore find wide application. Further studies are planned in which energy transfer between DODCI and its photoisomer will be investigated. A more detailed account of the results presented here will be given in a later publication.

ACKNOWLEDGEMENT

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REFERENCES